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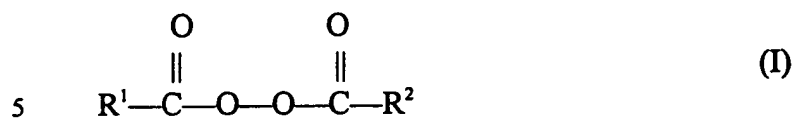
- (21) Application No.: 6-235338
15 (22) Filing Date: September 29, 1994
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(54) [Title of the Invention] **Liquid Bleach Composition**

(57) [Abstract]

25 [Structure] A liquid bleach composition comprising (a) 0.3 to 30 wt% H₂O₂, (b) 0.01 to 10 wt% diacyloyl peroxide represented by General Formula I, and (c) 0.1 to 30 wt% of at least one surfactant.

[Chemical Formula 1]



(where R¹ and R² are each independently a straight-chain or branched C₅ to C₂₁ alkyl group or the like, which may be joined by an ester linkage, amide linkage, or ether linkage).

10 [Effect] Results in far better storage stability.

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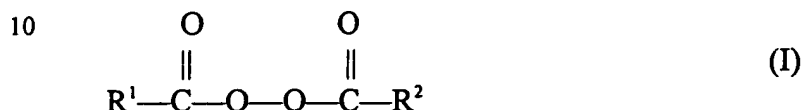
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[Claims]

[Claim 1] A liquid bleach composition, comprising the following components (a), (b), and (c):

- 5 (a): 0.3 to 30 wt% H₂O₂;
 (b) 0.01 to 10 wt% diacyloyl peroxide represented by General Formula I:

[Chemical Formula 1]



15 (where R¹ and R² are each independently a straight-chain or branched C₅ to C₂₁ alkyl or alkenyl group, which may be joined by an ester linkage, amide linkage, or ether linkage, or are an aryl group optionally substituted by a straight-chain or branched C₆ to C₂₀ alkyl or alkenyl group); and

- 20 (c) 0.1 to 30 wt% of at least one surfactant selected from the group consisting of anionic surfactants, nonionic surfactants, cationic surfactants, and amphoteric surfactants.

[Claim 2] A liquid bleach composition according to Claim 1, further comprising a bleach activator represented by General Formula II as component (d):

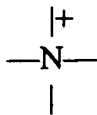
25 [Chemical Formula 2]



- 30 (where R³ is a straight-chain or branched C₅ to C₂₁ alkyl or alkenyl group, which may be joined by an ester linkage, amide linkage, ether linkage, or linkage represented by

35

[Chemical Formula 3]



or is an aryl group optionally substituted by a straight-chain or branched C₆ to C₂₀ alkyl or alkenyl group; Z is SO₃M or COOM, or is SO₃⁻ or COO⁻; M is a cation group; and m is 0 or 1).

10 [Claim 3] A liquid bleach composition according to Claim 1 or 2, further comprising a sequestrant as component (e).

[Detailed Description of the Invention]

15 [0001]

[Field of Industrial Application]

The present invention relates to a liquid bleach composition, and in particular to a liquid bleach composition with better storage stability, comprising a diacyloyl peroxide producing an organic peracid upon reaction with hydrogen peroxide.

20 [0002]

[Prior Art and Problems Which the Invention Is Intended to Solve]

Bleaches are classified into chlorine bleaches and oxygen bleaches. Chlorine bleaches, however, have limited application to fibers, cannot be used for colors or patterns, and have a distinctive odor. As a result, oxygen bleaches, which suffer from no such drawbacks, have become very popular. Sodium percarbonate and sodium perborate are used as powdered oxygen bleaches, while hydrogen peroxide is used as a liquid bleach.

30 [0003]

The bleaching power of oxygen bleaches is not as good as that of chlorine bleaches, however, making it necessary to use a variety of organic peracid precursors. Examples of such organic peracid precursors include O-acetylated substances such as glucose pentaacetate (GPAC), N-acylated substances such as tetracetyl ethylenediamine, and acid anhydrides such as maleic anhydride. The inventors previously found that compounds which produced organic peracids having quaternary ammonium groups upon

reaction with hydrogen peroxide were far better as organic peracid precursors, as disclosed in Japanese Unexamined Patent Applications (Kokai) 63-233969, 63-31566, 64-68347, and 1-190654. An example of an organic peracid precursor with anionic groups has furthermore been disclosed in Japanese Examined Patent Application (Kokoku) 63-12520.

[0004]

These organic peracid precursors are compounds that produce organic peracids upon reaction with hydrogen peroxide under mild conditions such as laundering conditions. They are thus generally unstable against hydrogen peroxide. For this reason, it is usually difficult to use such organic peracid precursors in the form of liquid bleaches, and they are thus commonly used in the form of compositions comprising a mixture of dry particles of organic peracid precursors and solid peracid salts for dry storage.

[0005]

A composition with better storage stability and activity at low temperatures, comprising a solid organic peracid precursor dispersed in an acidic solution containing hydrogen peroxide, has been disclosed as a liquid bleach composition with organic peracid precursors in Japanese Unexamined Patent Application (Kokai) 62-230897. Some drawbacks of this composition, however, are that the organic peracid precursor are dispersed and thus tend to precipitate during storage, resulting in considerable loss of the intended benefits when used.. The composition also involves the storage of organic peracid precursors in aqueous solution, resulting in gradual decomposition and the inability to obtain satisfactory bleaching power when used.

[0006]

As a result of extensive research on bleach compositions with better storage stability, the inventors provided the bleach composition comprising hydrogen peroxide, amphoteric surfactant, and organic peracid precursors disclosed in Japanese Unexamined Patent Application (Kokai) 6-49487. This composition still lacked satisfactory storage stability, however.

[0007]

An object of the present invention is to provide a liquid bleach with far better storage stability.

[0008]

[Means for Solving the Abovementioned Problems]

As a result of extensive research to remedy the aforementioned drawbacks, the inventors perfected the present invention upon finding that the aforementioned objectives could be obtained by a combination of surfactant and specific organic peracid precursors.

[0009]

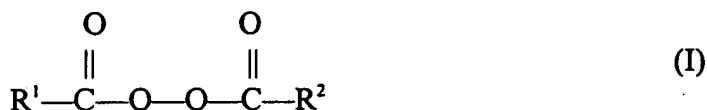
That is, the present invention is intended to provide a liquid bleach composition, comprising the following components (a), (b), and (c):

(a): 0.3 to 30 wt% H₂O₂;

(b) 0.01 to 10 wt% diacyloyl peroxide represented by General Formula I:

[0010]

[Chemical Formula 4]



[0011]

(where R¹ and R² are each independently a straight-chain or branched C₅ to C₂₁ alkyl or alkenyl group, which may be joined by an ester linkage (-COO- or -OCO-), amide linkage (-NHCO- or -CONH-), or ether linkage (-O-), or are an aryl group optionally substituted by a straight-chain or branched C₆ to C₂₀ alkyl or alkenyl group); and

(c) 0.1 to 30 wt% of at least one surfactant selected from the group consisting of anionic surfactants, nonionic surfactants, cationic surfactants, and amphoteric surfactants.

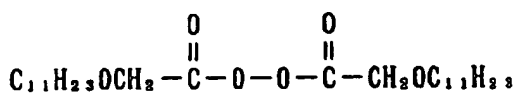
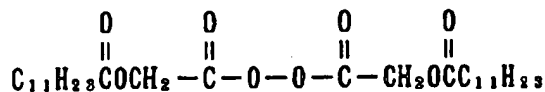
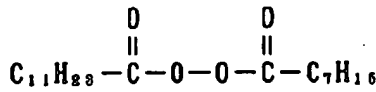
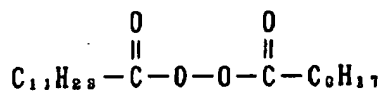
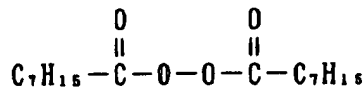
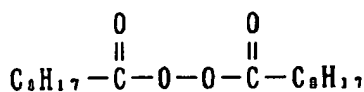
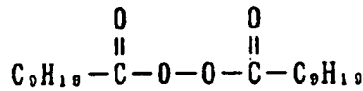
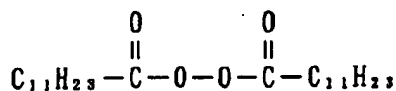
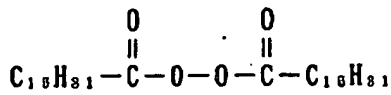
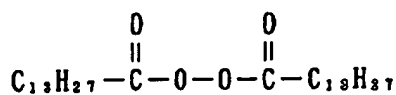
[0012] Component (b)

A diacyloyl peroxide represented by General Formula I is used as component (b). The following compounds are examples.

[0013]

[Chemical Formula 5]

[paste group of all formulas in middle of p. (3)]

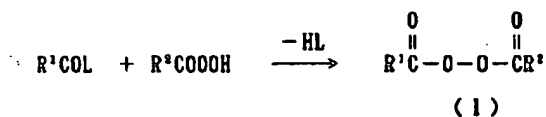


[0014]

Such diacyloyl peroxides can be synthesized in accordance with the following reaction scheme.

[0015]

[Chemical Formula 6]



[0016]

(where R¹ and R² are the same as above; and L is a leaving group). Examples of leaving groups in the aforementioned reaction scheme include those represented by

[0022]

[Chemical Formula 8]



[0023]

(where at least one of R^5 , R^6 , and R^7 is a straight-chain or branched C_6 to C_{22} alkyl or alkenyl group, which may be joined by an amide linkage, ester linkage, or ether linkage, and the rest are C_1 to C_3 alkyl or hydroxyalkyl groups; R^8 is a straight-chain or branched C_1 to C_6 alkylene group optionally substituted by a hydroxy group; and Y^- is SO_3^- or COO^-).

[0024]

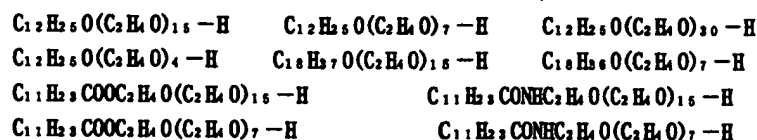
[Chemical Formula 9]



[0025]

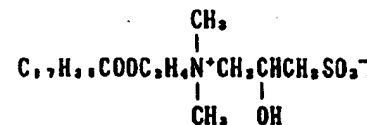
(where R^5 , R^6 , and R^7 are the same as above; R^9 is a C_1 to C_3 alkyl group or hydroxyalkyl group; and X^- is an anion group (such as halogen ion (Cl or Br), C_3SO_4^- , $\text{C}_2\text{H}_5\text{SO}_4^-$)).

The following are examples of surfactants represented by General Formula III:



[Chemical Formula 10]

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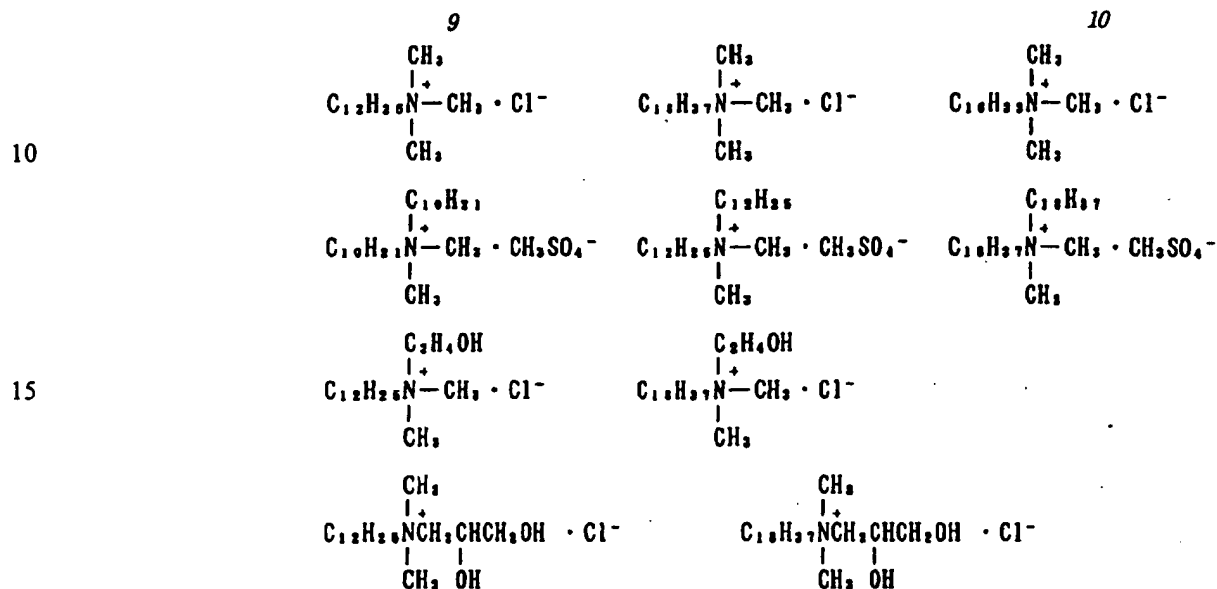


[0027]

The following are examples of surfactants represented by General Formula V:

[0028]

5 [Chemical Formula 11]



[0029] Liquid Bleach Composition

The bleach composition of the present invention comprises 0.3 to 30 wt%, preferably 0.5 to 20 wt%, and even more preferably 0.5 to 10 wt%, component (a), and
 25 0.01 to 10 wt%, preferably 0.1 to 10 wt%, and even more preferably 0.5 to 5 wt%, component (b). The content of component (c) is 0.1 to 30 wt%, preferably 0.1 to 20 wt%, and even more preferably 1.0 to 20 wt%.

[0030]

30 The blending ratio between components (b) and (c) is a weight ratio (b/c) of 1/50 to 5/1, preferably 1/20 to 2/1, and more preferably 1/10 to 1/1.

[0031]

35 Less than 0.3 wt% component (a) will fail to yield satisfactory bleaching performance. More than 30 wt%, on the other hand, will run the risk of poor hydrogen peroxide storage stability.

[0032]

Less than 0.01 wt% component (b) will fail to yield satisfactory bleaching performance, whereas more than 20 wt% tends to cause fading of colored patterns.

5 [0033]

The storage stability will suffer when the content of component (c) is outside the range of 0.5 to 30 wt%.

[0034]

10 Good storage stability cannot be achieved outside the above range for the blending ratio between components (b) and (c).

[0035]

15 A bleach activator represented by General Formula II can be added as component (d) to improve the bleaching performance of the composition in the present invention.

[0036]

[Chemical Formula 12]

20

[paste II, middle right of p. (6)]

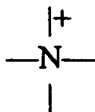
[0037]

25 (where R³ is a straight-chain or branched C₅ to C₂₁ alkyl or alkenyl group, which may be joined by an ester linkage, amide linkage, ether linkage, or linkage represented by

[0038]

[Chemical Formula 13]

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[0039]

or is an aryl group optionally substituted by a straight-chain or branched C₆ to C₂₀ alkyl or alkenyl group;

5 [0040]

Z is SO₃M or COOM, or is SO₃⁻ or COO⁻; M is a cation group; and

[0041]

m is 0 or 1).

10

The content of component (d) is 0 to 20 wt%, preferably 0.1 to 15 wt%, and more preferably 0.5 to 10 wt%.

[0042]

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More than 20 wt% component (d) tends to result in fading of colored patterns.

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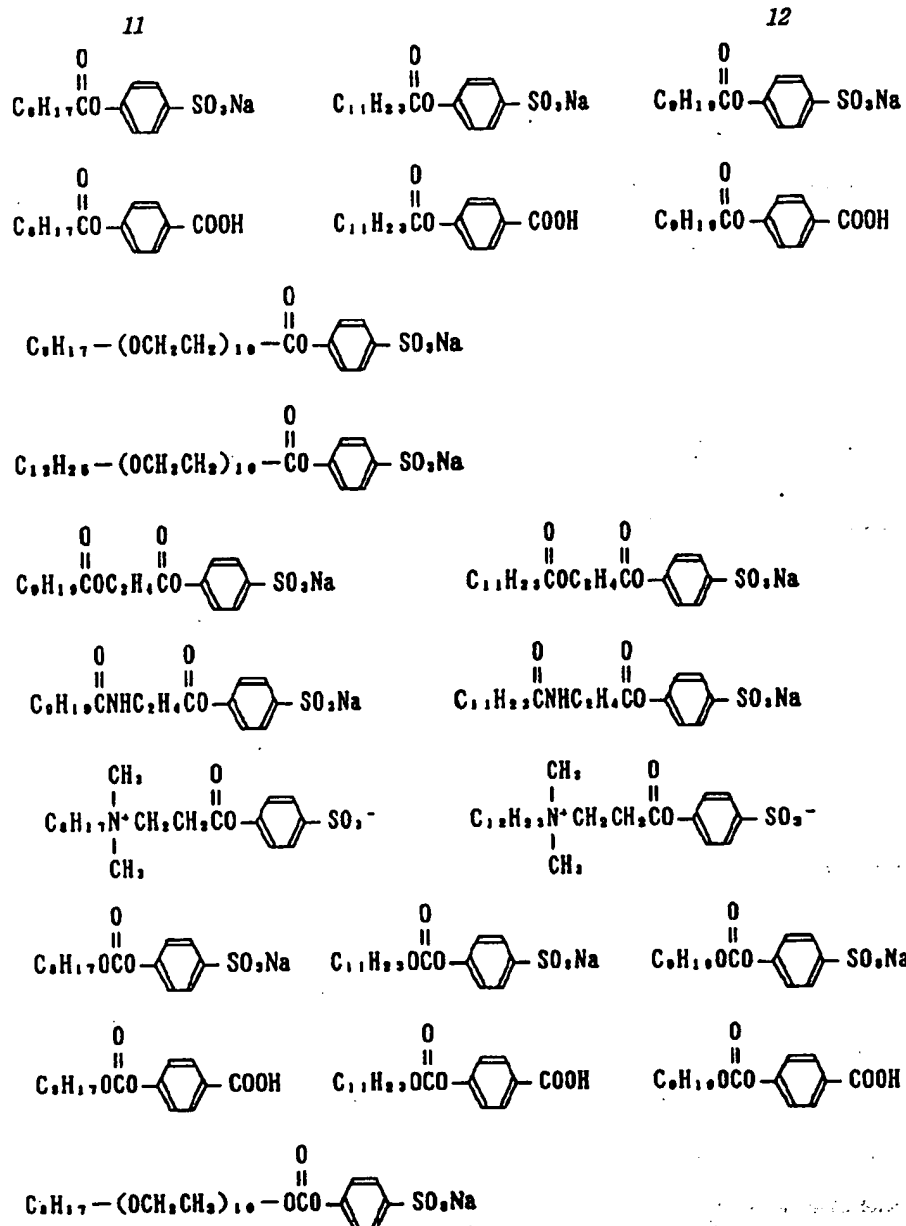
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[0043]

The following are examples of desirable compounds for bleach activators represented by General Formula III:

5 [0044]

[Chemical Formula 14]



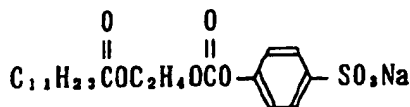
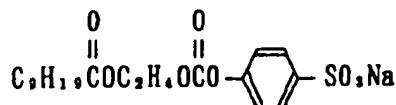
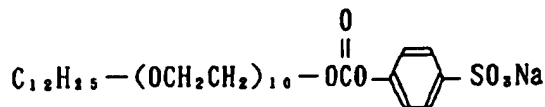
[0045]

[Chemical Formula 15]

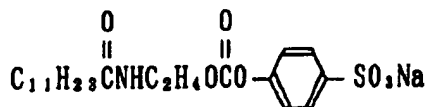
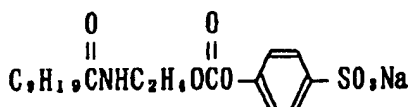
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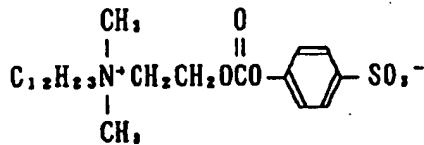
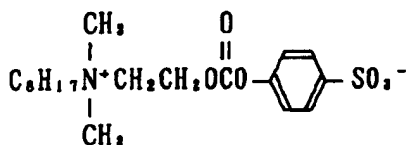
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[0046]

A sequestrant can also be blended as component (e) in the present invention.

Examples of sequestrants include:

20

1) phytic acid and other such phosphate compounds, or alkali metal salts, alkaline earth metal salts, ammonium salts, or alkanolamine salts

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2) ethane-1,1-diphosphonic acid, ethane-1,1,2-triphosphonic acid, ethane-1-hydroxyl-1,1-diphosphonic acid, ethane-1-hydroxy-1,1,2-triphosphonic acid, ethane-1,2-dicarboxy-1,2-diphosphonic acid, methanhydroxyphosphonic acid, and similar phosphonic acids or their alkali metal salts, alkaline earth metal salts, ammonium salts, or alkanolamine salts

30

3) polycarboxylates comprising acrylic acid, maleic acid, itaconic acid, aconitic acid, methacrylic acid, fumaric acid, 2-hydroxyacrylic acid, citraconic acid and similar polymers or copolymers of two or more, where the average molecular weight is 500 to 100,000, and part or all of the carboxyl groups are alkali metal salts, alkaline earth metal salts, ammonium salts, or alkanolamine salts

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4) 2-phosphonobutane-1,2-dicarboxylic acid, 1-phosphonobutane-2,3,4-tricarboxylic acid, and α -methylphosphonosuccinic acid and similar phosphonocarboxylic acids or their alkali metal salts, alkaline earth metal salts, ammonium salts, or alkanolamine salts

5) aspartic acid, glutamic acid, glycine and similar amino acids or their alkali metal salts, alkaline earth metal salts, ammonium salts, or alkanolamine salts

6) nitrilotriacetic acid, iminodiacetic acid, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, glycol ether diaminetetraacetic acid, hydroxyethyliminodiacetic acid, triethylenetetraminehexaacetic acid, djenkolic acid and similar aminopolyacetic acids or their alkali metal salts, alkaline earth metal salts, ammonium salts, or alkanolamine salts

7) diglycolic acid, oxysuccinic acid, carboxymethyloxysuccinic acid, citric acid, lactic acid, tartaric acid, oxalic acid, malic acid, oxydisuccinic acid, gluconic acid, carboxymethylsuccinic acid, carboxymethyltartaric acid and similar organic acids or their alkali metal salts, alkaline earth metal salts, ammonium salts, or alkanolamine salts

8) alkali metal salts, alkaline earth metal salts, ammonium salts, or alkanolamine salts of aluminosilicates such as zeolite A

[0047]

At least one selected from 2), 3), 6), or 8) is particularly preferred. The sequestrant is used in an amount of 0.0005 to 30 wt%, and preferably 0.1 to 20 wt%, relative to the bleach detergent composition.

[0048]

Commonly added ingredients can also be used in addition to the aforementioned components in the present invention. Examples include alkali agents such as sodium carbonate; whiteners for enhancing the bleaching effects on the bleached fibers, such as Tinopal CBS (by Ciba Geigy), Tinopal SWN (by Ciba Geigy), and C.I. Fluorescent Whiteners 28, 40, 61, and 71; and common enzymes (such as cellulases, amylases, proteases, lipases) for enhancing the bleaching performance.

[0049]

The present invention can also include small amounts of various other additives, including colorants such as dyes and pigments, fragrances, silicones, antibacterials, and UV absorbents.

[0050]

The composition of the present invention is obtained by dissolving or dispersing components (a) through (c) or (a) through (e) in tap water or deionized water. The optional components are then added in suitable amounts therein.

[0051]

[Effects of the Invention]

The present invention provides a liquid bleach with far better storage stability.

[0052]

[Examples]

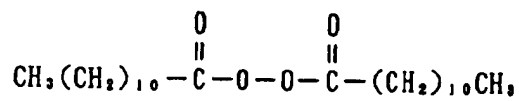
The present invention is illustrated in the following examples, but the present invention is not limited to these examples alone.

[0053] Examples 1 through 6, and Comparative Examples 1 through 5

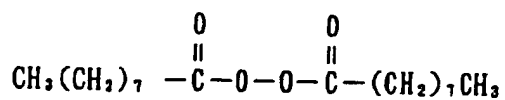
Liquid bleaches were prepared with the blends shown in Table 1 using the following components (b-1) and (b-2) as component (b), components (c-1) through (c-5) as component (c), components (d-1) and (d-2) as component (d), and component (e-1) as a chelator. The results of tests on the bleaching effects and storage stability are given in Table 1. Compound (b-1) was commercially available lauroyl peroxide (Nacalai Tesque). Compound (b-2) was prepared by a reaction between nonanoyl sodium oxybenzenesulfonate and pernonanoic acid in aqueous solution. The compositions in Table 1 were adjusted to pH 2 with 0.5 N sulfuric acid aqueous solution.

[0054]

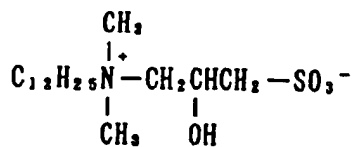
[Chemical Formula 16]



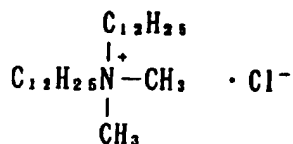
(b-1)



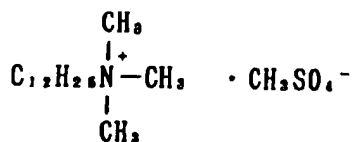
(b-2)



(c-1)



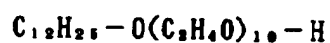
(c-2)



(c-3)

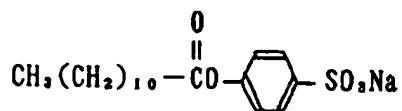


(c-4)

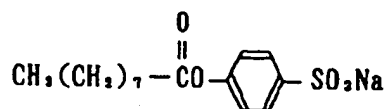


(c-5)

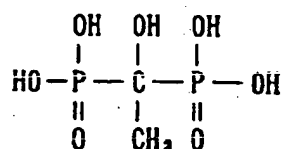
[0055]



(d-1)



(d-2)



(e-1)

[0056] Evaluation of Storage Stability

The amount of bleach activator producing organic peracid in the sample was measured, and the percentage of remaining available bleach activator was calculated by the following equation.

[0057]

[Numerical Formula 1]

$$\text{percentage (\%) available bleach activator remaining} = \frac{\text{amount of available bleach activator after storage}}{\text{amount of available bleach activator before storage}} \times 100$$

[0058] Bleaching Performance

40 mL bleach composition in Table 1 was added to 2 L of 0.133% commercially available detergent aqueous solution (pH 10.2), and five sheets of tea-stained fabric prepared in the manner described below were dipped for 15 minutes each. They were then rinsed with tap water and dried, and the bleaching rate was determined by the following equation.

[0059] Bleaching rate of tea-stained fabric

[0060]

[Numerical Formula 2]

$$\text{Bleaching rate (\%)} = \frac{\text{reflectance after bleaching} - \text{reflectance before bleaching}}{\text{reflectance of white fabric} - \text{reflectance before bleaching}} \times 100$$

[0061]

The reflectance was determined using a 460 nm filter with an NDR-101DP by Nippon Denshoku Kogyo

[0062] Preparation of tea-stained fabric

80 g Nitto tea (Yellow Package) was boiled for about 15 minutes in 3 L deionized water, it was then strained with desized bleached cotton, and cotton fabric #2003 was then dipped in the liquid and boiled for about 15 minutes. It was taken from the flame and allowed to stand for about 2 hours and then allowed to dry naturally. It was then washed with a washing liquid until no color ran. It was then dehydrated, pressed, and cut into 10 cm × 10 cm test pieces for tests.

10 [0063]
[Table 1]

		Example						Comparative Example				
		1	2	3	4	5	6	1	2	3	4	5
Liquid oxygen bleach composition (wt%)	hydrogen peroxide	5	5	5	5	5	5	5	5	5	5	5
	b-1	1		1	1	1		1		1		
	b-2		1				1		1		1	
	c-1	5										5
	c-2		2.0		2.0							
	c-3			2.0		2.0						
	c-4				10		10					
	c-5					10						
	d-1			0.5		0.5				0.5		
	d-2				0.5		0.5				0.5	
	e-1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	deionized water	bal.	bal.	bal.	bal.	bal.	bal.	bal.	bal.	bal.	bal.	bal.
	pH	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Storage stability	temp. (°C)	50	50	50	50	50	50	50	50	50	50	50
	humidity (%)	80	80	80	80	80	80	80	80	80	80	80
	Time stored (months)	5	5	5	5	5	5	5	5	5	5	5
	Remaining available bleach activator (%)	95.0	94.9	94.1	94.1	94.4	95.1	10.1	9.8	15.5	11.2	
Bleaching	Before storage (%)	15.1	14.9	15.2	14.8	14.4	15.7	9.9	9.9	9.8	9.9	4.1
	After storage (%)	13.9	13.7	14.6	13.4	13.0	14.5	4.3	4.1	4.9	5.1	4.0